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Penetration of methyl bromide, sulfuryl fluoride, ethanedinitrile and phosphine into timber blocks and the sorption rate of the fumigants

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Abstract

To evaluate timber fumigants alternative to the ozone-depleting methyl bromide (MB), pinewood (Oregon, *Pseudotsuga menziesii*) blocks (10 cm × 10 cm × 30 cm) were fumigated in a stainless steel chamber (30.0 L). The timber blocks were fumigated at 48 mg L^{-1} of MB, sulfuryl fluoride (SF) and ethanedinitrile (C_2N_2) and 1 mg L^{-1} of phosphine (PH_3) for 48 h. During fumigation, 70% MB, 35% SF, 63% C_2N_2 and 25% PH_3 were absorbed by the timber block. At 6-h exposure, the concentrations of SF, PH_3 and C_2N_2 in the headspace of the chamber were stable. Each fumigant penetrated to all parts of the block, but the speed and extent of penetration was different. The fumigants that most rapidly achieved an even concentration throughout the block and chamber were PH_3 and C_2N_2. The maximum variation of MB, SF, C_2N_2 and PH_3 concentration between the chamber and gas port (15 cm) was 81.3, 11.8, 1.5 and 9.3% at 24 h exposure and 76.8, 9.3, 0.5 and 1.1% at 48 h exposure respectively. Possible alternative fumigants to MB need to penetrate timber at least as well as MB; SF, PH_3 and C_2N_2 met this criterion.

Keywords: Timber, fumigation penetration, alternative fumigants, methyl bromide, sorption of fumigant

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1. Introduction

Fumigation has become the accepted practice to disinfest and disinfect timber and wooden structures. Fumigants can reach points in wood bundles and, to varying degrees, inside wood that other pesticides do not easily reach. Fumigants such as methyl bromide (MB) and sulfuryl fluoride (SF) have been used to control wood-destroying organisms (Hunt, 1949; Su and Scheffrahn, 1986). Sulfuryl fluoride has been used to control wood-destroying termites in structures for more than 50 years (Su and Scheffrahn, 1986). Methyl bromide has been widely used for quarantine treatment of timbers, wooden packaging and logs for many years (Ren, 1996; Ren et al., 1997; Ren et al., 2006). However, MB is being withdrawn as an ozone depleting substance under the Montreal Protocol (UNEP, 2006). Potential alternative fumigants such as phosphine (PH_3) and ethanedinitrile (C_2N_2) were therefore re-evaluated or developed to replace MB for rapid fumigation and quarantine treatment of timber and wood packaging. Phosphine has world-wide registration as a fumigant for grains. Fumigation with phosphine requires long exposure periods (> 5 days) to control eggs and pupae of many species. Ethanedinitrile is a patented alternative fumigant (patented under the chemical name cyanogen) and has been shown to have potential as a quarantine treatment for timber (Desmarchelier and Ren, 1996; Viljoen and Ren, 2001; Wright et al., 2002; Ren et al., 2006). The penetration of the fumigants into timber and the sorption rate of the fumigants are major uncertain factors that affect effective fumigation (Su and Scheffrahn, 1986; Ren 1996; Ren et al., 1997). Stewart (1957) demonstrated that conifer-wood sawdust packed into a column 28 cm in height was penetrated by MB and SF added to the top, sufficiently to kill termites in a fumigation chamber placed under the column. Sulfuryl fluoride was shown to penetrate the packed sawdust column at a faster rate, and further evaluation of materials, including timber, clearly demonstrate that SF penetrates more readily than MB (Kenaga, 1957; Kenaga, 1961; Derrick et al., 1990). Scheffrahn et al. (1992a) studied the diffusion of MB through structural wood matrices (wood discs of 20mm width). Methyl bromide was unable to achieve lethal concentrations across four out of four hydrated woods or across at least two of five dry woods. Liese et al. (1981) and Liese and Ruetze (1985) studied penetration of MB into oak log sections and showed that axial distribution of MB was <5cm within 24 hours. Carbonyl sulfide penetrated timber

blocks better than MB, and was less sorbed on dry timber blocks (Ren, 1996; Ren et al., 1997).

In this paper we report comparative results for the penetration of MB, SF, C_2N_2 and PH_3 through timber blocks, concentration × time (*Ct*) products in the fumigation chamber and in the timber block core, and sorption rate of the fumigants on timber under laboratory controlled experimental conditions.

2. Materials and Methods

2.1. Fumigation chamber

The fumigation chamber (40 cm × 40 cm × 18.75 cm) was made from stainless steel and fitted with 2 gas sampling ports (Figs 1 and 2). The net volume of the chamber was 30.0 L. The top plate of the fumigation chamber was designed to accommodate 2 timber blocks which were secured on the plate with two clamps for each block (Fig. 1). Two timber blocks (2 × 3.0 L = 6.0 L) were placed in the chamber to achieve a loading ratio of 20.0%. The design loading ratio of 20% was based on a fully loaded container of pallets (the pallet timber taking <20% of the container volume). In the case of commercial container fumigation, the timber pallet often only occupies less than 5% of the container volume. A 20% loading ratio is therefore designed to reflect the treatment of pallets only (i.e. a container fully loaded with pallets).

2.2. Prepare timber blocks

Pinewood (Oregon Douglas-fir, *Pseudotsuga menziesii* (Mirb.) Franco) was used as the source of the timber blocks for testing. The timber blocks (10 cm × 10 cm × 30 cm) were cut with one axis on the longer side parallel to the grain and cut at least 5 cm from the end of the piece of lumber (Fig. 1). The timber blocks had no visible cracks at the time of preparation. Before starting the fumigation testing, the timber blocks were conditioned for 2 months at 25±2°C and 60% relative humidity (r.h.).

The major route of penetration of methyl bromide into softwood timber blocks is with the grain of the timber block rather than across the grain (Brenton, 1990; Cross, 1991; Ren, 1996; Ren et al., 1997). Therefore, each timber block had one set of sampling holes fitted with gas sampling ports (Figs 1 and 2). A set of gas

monitoring holes was placed at 5, 10 and 15 cm from each end of the timber block along the middle of the timber block. In order to take gas samples during the fumigation process out of the timber blocks, the top plate of the fumigation chamber was furnished with 10 gas sample probe fittings, sealed by screwed-on septa as commonly used in gas chromatographs. The holes were of 1.5 mm i.d. and were lined with gas sampling probes (5 cm long × 3.0 mm o.d.) to facilitate sampling of gas directly from the centre of the block and to ensure at least 4-5 mm between the end of the probe and bottom of hole.This made the sampling volume more than 200 µL (Fig. 2). The gas sample system (gas sample probe and sealing) was fitted into the timber block before placing into the top plate of the fumigation chamber. The sample port septum and cap were fitted after hooking the timber block to the top plate (Fig.2).

Moisture contents and densities of timber blocks were determined by standard test methods (American Standard Test Methods, 1981 and 1983). The moisture content of the blocks was 7.8%, and their specific gravity was 0.44-0.45 g cm^{-3}. All experiments were conducted at 23-25°C.

2.3. Fumigant, dosages and exposure time

Methyl bromide (98.5% MB and 1.5% air) and ethanedinitrile (98.0% C_2N_2 and 2.0% air and CO_2) were sourced from BOC Gases Australia. Sulfuryl fluoride (99.8% SF and 0.2% CO_2) was supplied by Dow AgroSciences LLC, Atascadero, CA. Phosphine (85.0% PH_3 and 15.0% air and CO_2) was laboratory prepared by the FAO method (FAO, 1975).

The purity of MB, SF, C_2N_2 and PH_3 was determined using a GOW-MAC gas density balance (GOW-MAC Instrument Co., Madison, N.J.) after separation of the gases on a 1 m × 5 mm i.d. Porapak Q 100/120 mesh (Alltech Associates, Cat. No. 2702) column at 105°C with a carrier flow (N_2) of 150 mL min^{-1}. The reference gas used was tetrafluoroethane (> 99.9%), which was supplied by ACTROL Ltd, Australia.

The dosage of MB of 48 mg L^{-1} was based on the AQIS Methyl Bromide Fumigation Standard (2008). The dosage of 48 mg L^{-1} for SF and C_2N_2 was chosen partly for comparison with MB of their penetration and sorption into timber and partly because these fumigants at these doses control most timber pests (Barak et

al., 2002; Ren et al., 2006). For PH_3, a dosage of 1 mg L^{-1} was used as this is consistent with the current dosage used for on-board in-transit timber fumigation (Brash et al., 2008) and because it is below the explosion limit. The volume is calculated from that of the total enclosure, not that occupied by the timber. Before dosing, to avoid changes in pressure, a volume of air was removed from the fumigation chamber equivalent to the dosage volume. The dosage (calculated by Eq. 1, Ren et al., 2006) was injected into the fumigation chamber using a gas-tight syringe. Each fumigant treatment was in duplicate (n=2). The period of fumigation was 48 hours. After fumigation, the top of the chamber was opened and aired for two days. All experiments were conducted at 23-25°C.

The dosages and required volumes for the fumigant concentrations were calculated from Eq. 1 calibrated to the laboratory temperature and pressure.

$$\mathbf{V_f} = (1-\frac{T}{273})\ (\frac{1.7\times10^4\times C\times V}{P\times M\times N}) \qquad \textbf{Eq. 1.}$$

Where: ***V*** is volume of fumigation container (L)

P is pressure (mm Hg)

T is temperature (°C)

C is the intended concentration of fumigant (mg L^{-1})

$\mathbf{V_f}$ is dosage volume of fumigant (ml)

M is molecule weight of fumigant, and

N is purity of gas (%)

2.4. Measurement of fumigant concentrations by GC

Methyl bromide was determined on a Varian 3400 GC (Varian Instruments, Sunnyvale, CA), equipped with a flame ionisation detector. Separation was achieved for MB and methyl chloride on a 30 m × 0.53 mm i.d. GS-Q megabore column (J&W Scientific; Folsom, CA; Cat. No. 115-3432), at 140°C with a carrier flow (N_2) of 4.6 mL min^{-1} at 6.0 psi. Phosphine and SF were determined on a Varian 3800 GC (Varian Instruments, Sunnyvale, CA), equipped with a flame photometric detector, after separation on a 30 m × 0.53 mm i.d. × 1.4 µm DB-624 megabore column (J&W Scientific; Cat. No. 122-1334), at 90°C with a carrier flow (N_2) of 5.0 mL min^{-1} at 5.0 psi. Ethanedinitrile was analyzed using a SRI 8610C gas

chromatograph (GC) equipped with a nitrogen and phosphorus detector after isothermal separation on a 15 m × 0.53 mm i.d. GS-Q megabore column (J&W Scientific; Cat. No. 115-3432) at an oven temperature 90^{o}C and a carrier flow (N_2) of 4.0 mL min^{-1} at 3.8 psi.

2.5. Preparation of gas standard

Gas standards were used as external standards for calculation of fumigant concentrations. They were prepared by injecting concentrated fumigant into an Erlenmeyer flask (1-L) containing 5-7 glass beads (2-3 mm diameter) for stirring the fumigant. Concentrations of standards were close to those in the chamber and within the range where the GC response was proportional to the concentration. Each flask was fitted with a ground glass joint (Bibby Sterilin Ltd., Staffordshire, UK, CNB 19 UB ST5), the top drawn out to a 6 mm o.d. tube fitted with a half-hole septum (Alltech Associates, Sydney, Australia, Cat. No. 6526). This system is similar in design to a commercial adaptor (Bibby Sterilin Ltd., MF 10/3). The volume of each Erlenmeyer flask and inlet system was measured from the weight of water required to fill the container. The volume of fumigant used was calculated from Eq. 1.

2.6. Measurement of fumigant in the fumigation chamber and in the timber block core

Before dosing, the gas-tightness of the fumigation chamber was checked by pressurising and monitoring the gas pressure using a digital manometer (Model EMA 84, Halstrup-Walcher GmbH, Kirchzarten, Germany). Air (70 mL) was injected into the chamber with 100 mL syringe (Alltech Associates, Sydney, Australia, Cat. No. 009770SGE), and left overnight; there was no change in pressure over this period. A volume of air was removed from the fumigation chamber equivalent to the dosage volume to avoid changes in pressure. The dosage was injected into the fumigation chamber using a gas-tight syringe. After dosing, the first set of readings was taken within half an hour and repeated sets of readings were taken approximately 1, 2, 4, 6, 8, 24 and 48 h later. The same sampling injection volume was used for samples and standards. For assessment of the penetration into timber blocks and proportion of flow with and across the grain, the

ratio of in-timber block to fumigant concentration in the test chamber space provides a measure of penetration.

The volume of gas samples taken from the end of each gas sample port and injected into the GC using a 100-µL syringe (Alltech Associates, Sydney, Australia, Cat. No. 005250SGE) was 40 µL. Similar volumes were used with the standard injections. The concentration of the standard was as close as possible to that of the test sample injection.

2.7. Determination of Concentration× time products (Ct) of fumigant in the fumigation chamber and in the timber block core

The concentrations of fumigants were monitored at time intervals over the exposure period (48 hours) and were used to calculate the product *Ct* = Concentration × time. The *Ct* products were calculated from Eq. 2.

$$Ct = \sum (C_i + C_{i+1})\,(t_i - t_{i-1})/2 \qquad \textbf{Eq.2.}$$

Where: **C** is fumigant concentration (mg L^{-1})

t is time of exposure (hours)

i is the order of measurement

Ct is concentration × time products (mg h L^{-1})

2.8. Statistical Analysis

We conducted separate analysis for each observation sample port (5, 10 and 15 cm) at the different exposure times. Differences in fumigant concentration at 5, 10 and 15 cm in two timber blocks in the same chamber and between the duplicate treatments (*n=4*) were analyzed by analysis of variance (ANOVA), using procedures of SAS (version 9.0, SAS Institute 2002). The variations (Standard Deviation) of fumigant concentration and *Ct* products at different sample ports in comparison with average readings were analysed by Microsoft Excel 2007.

3. Results and discussion

3.1. Penetration of fumigant through timber blocks

The fumigant penetration into timber blocks is shown in Fig. 3. Each fumigant penetrated to all parts of the block, but the speed and extent of penetration was different.

The concentration of MB did not reach half of the chamber concentration. Concentrations of MB in the core of the timber block were consistently lower than in the chamber ($P < 0.0001$), and had not equalised with the chamber at 5, 10 and 15 cm distance into the block during the 48-h exposure period, e.g. at 48-h fumigation, the concentrations of MB in the chamber, and at the 5, 10 and 15 cm ports were 19.0, 14.0, 12.0 and 4.4 mg L^{-1}. During 48 hours fumigation, the concentration of MB decreased with increasing distance of penetration (*P=0.0001*; $F_{3,24}$=27.39). The variation ($n = 4$, SD < 6.5%) of MB concentration between the chamber and at each port (5, 10 and 15 cm) was 25.0, 38.3 and 81.3% at 24 h exposure (*P=0.003*; $F_{3,3}$=27.39) and 26.3, 36.8 and 76.8% at 48 h exposure *P=0.0021*; $F_{3,3}$=27.39) respectively. Complete penetration occurs when all in-timber block concentrations are the same as those in the chamber. Penetration solely across the grain would be shown by simultaneous increase in in-timber block concentrations at each sampling point. Penetration with the grain would be shown by an increase in concentration at 5 cm from each end occurring at a much faster rate than at the other sampling points. In the initial stages of fumigation, the decline in concentrations with distance from the near end (5 cm) confirmed penetration was predominantly with the grain (*P=0.007*; $F_{3,24}$=17.64). Had distribution across the grain been the predominant method of penetration, concentrations at each port would be the same, as each is 5 cm equidistant from the long side. This result is consistent with the results from Peters (1990), Cross (1991), Ren (1996) and Ren et al. (1997). The information gained on MB as a timber fumigant is of interest as it shows it has poor penetration into timber blocks and it does not penetrate across the grain. For example, between 24 and 48 h the changes of MB concentration in the chamber decreased by 6 mg L^{-1}, increased 4 and 3 mg L^{-1} at the 5 and 10 cm sampling ports and decreased 1 mg L^{-1} at 15 cm. That is, there was no significant increase in core concentration after 24-h exposure.

For SF, the stable concentrations at each port and in the chamber were achieved at 28 h of fumigation. However, the in-timber block concentration of SF was consistently lower than in the chamber, and had not equalised with the chamber (30 mg L^{-1}) at 5 cm (29 mg L^{-1}), 10 cm (28 mg L^{-1}) or 15 cm (27 mg L^{-1}), during the 48-

h exposure period (*P<0.001*; $F_{3,24}$=39.23). The variation (*n = 4*, SD < 5.1%) of SF concentration between the chamber and each port (5, 10 and 15 cm) was 9.4, 10.1 and 11.8% at 24 h exposure and 9.5, 9.0 and 9.3% at 48 h exposure respectively. Thus the major penetration of SF into timber blocks was with the grain rather than across the grain (*P=0.02*; $F_{3,24}$=6.00). It is clear that SF penetrates timber block more readily than methyl bromide, which is consistent with the findings of Stewart (1957), Kenaga (1957, 1961) and Derrick et al. (1990).

For PH_3, within 1 h, the concentration at the 15 cm port was half of that in the chamber. The variation (*n = 4*, SD < 3.3%) of PH_3 concentration between the chamber and each port (5, 10 and 15 cm) was 1.5, 5.2 and 9.3% at 24 h exposure and 1.0, 1.1 and 1.1% at 48 h exposure respectively. The penetration rate of PH_3 was similar to that of SF. At 48 h fumigation, the equilibrium concentration of PH_3 in the chamber and at each sample port was achieved and had equalised at levels of 0.9 mg L^{-1} (*P=0.04*; $F_{3,24}$=4.42; df=3).

For C_2N_2, the penetration character was different from that of MB, SF and PH_3. Within 1 h, the concentration at the 15 cm port was half of that in the chamber. After 6 h fumigation, the equilibrium concentration of C_2N_2 in the chamber and at each port was achieved and had equalised at levels of 25 mg L^{-1} (*P<0.0001*; $F_{3,27}$=48.57) with variation of less than 1.5% between the chamber and each port (5, 10 and 15 cm). At the end of fumigation, the equalised concentration at all sample ports was maintained at 22 mg L^{-1} (*P=0.0154;* $F_{3,27}$=10.13;). The variation (*n = 4*, SD < 0.2%) of C_2N_2 concentration between the chamber and each port (5, 10 and 15 cm) was 0.5% (*P=0.0324;* $F_{3,27}$=7.09). The penetration of C_2N_2 was rapid and the distance into the timber block had minimal influence on the rate that equilibrium was attained (*P=0.0002*; $F_{3,27}$=23.68;). As previously reported by Desmarchelier and Ren (1996), the penetration of C_2N_2 into timber blocks occurred with and across the grain of the timber block.

3.2. Sorption of fumigant on timber block

The concentrations of each fumigant declined rapidly, as the fumigants were sorbed by the timber block (Fig. 4). After 10 h, concentrations remained stable for all fumigants except MB where the chamber concentration continued to decline. The stable concentration in the chamber, expressed as a ratio of the applied concentration, was 68% for SF, 39% for C_2N_2 and 78% for PH_3 (*P=0.0007*,

$F_{3,27}$=17.77). Methyl bromide continued to decline, with approximately 53 and 62% of the initial chamber concentration being sorbed by the timber block at 8 and 24 h respectively. After 24 h up to completion of 48-h exposure, the loss of MB by sorption was less than 8%, indicating that physical sorption of MB by the timber block had almost reached saturation within the initial 24 h (*P=0.09*; $F_{3,27}$=3.04).

3.3. Concentration× time products (Ct) of fumigant in fumigation chamber and in the timber block core

The desirable quality of evenness of distribution can be assessed by measuring the time for concentrations in the three timber ports and the chamber to obtain the same value (equilibrium). Equilibrium *Ct* products were achieved at 24 h for PH_3 and C_2N_2, but were not reached after 48 h for MB and SF (Fig. 5). The *Ct* products for SF had equalized in the three timber ports after 24 h but remained below the chamber value. All four values of MB remained different.

The importance of uniform *Ct* products is shown in Table 1 which compares measured *Ct* products with those required to control, at two temperatures, larvae of the Asian Longhorn beetle *Anoplophora glabripennis* Motschulsky (Coleoptera: Cerambycidae) (Barak et al., 2002; Ren et al., 2006). The measured *Ct* product of MB at 5cm is sufficient for control at 21.1°C, but not at 10°C and the product at 15 cm is insufficient at each temperature. At both 5 and 15 cm, the *Ct* product of SF controls all stages at the higher but not at the lower temperature. Ethanedinitrile controls all stages at each temperature. As illustrated in Table 1, evenness of penetration is only one part of a picture made complex by the variety of insect species and the effect of conditions on the toxicity of fumigants, but it is an essential part where insects are present within the wood, rather than only on the surface.

In general, fumigation with an initial dosage of 48 (MB, SF and C_2N_2) or 1 (PH_3) mg L^{-1} for a 24-hour exposure achieve *Ct* products that kill almost all stages of timber insect pests at warm temperatures (Barak et al., 2002; Ren et al., 2006). Some egg stages need even higher *Ct* products for SF and PH_3, eg. *Ct* products of 470 mg h L^{-1} (SF**)** did not eradicate eggs of *Lyctus brunneus* (Stephens) and the anobiid beetle *Euvrilletta peltate* (Harris) (Outram, 1967; Su and Scheffrahn, 1990; William and Sprenkel, 1990). For C_2N_2, the *Ct* product

during 24 hours exposure kills nematodes and wood pathogens (Ren et al., 2002; Wright et al., 2002; Mattner et al., 2003; Ren 2007; Ren and Lee 2008).

Conclusions

Based on rate and extent of penetration, C_2N_2 and PH_3 are clearly the preferred fumigants for timber, following by SF. Sulfuryl fluoride, C_2N_2 and PH_3would provide greater efficacy when used for the treatment of timber to control insect pests. Ethanedinitrile is a fumigant with the potential to replace MB for control of insects, nematodes and wood pathogens. The results presented here could provide the evidence to generate a timber fumigation protocol.

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Captions for figures

Fig. 1. Schematic representation of a sealed fumigation chamber (40 cm × 40 cm × 18.75 cm) and the organisation inside the chamber; timber blocks (10 cm × 10 cm × 30 cm) are in the position for testing and sample ports are 5, 10 and 15 cm from each end of the block.

Fig. 2. Schematic representation of sealing, gas sample probe fitting and sample port.

Fig.3. Penetration of fumigants through the timber blocks (−●−, headspace of chamber; −Δ−, 5 cm; −○−, 10 cm; and −▲−, 15 cm)

Fig. 4. Concentration of fumigant in the headspace of the fumigation chamber (−Δ−, methyl bromide; −▲−, sulfuryl fluoride; −●− ethanedinitrile and −○−, phosphine), where C/Co is the ratio of concentration of fumigant (*C*) in the headspace to the calculated applied concentration (*Co*).

Fig. 5. Concentration × time (*Ct*) products of fumigant in the core (5, 10 and 15 cm) of the timber block vs time, with an initial dosage of 48 (MB, SF and C_2N_2) and 1 mg L^{-1} (PH_3).

Table 1. *Ct* products after 48 h at two depths in a timber block and those required to control *Anoplophora glabripennis* Motschulsky (Coleoptera: Cerambycidae) (larvae).

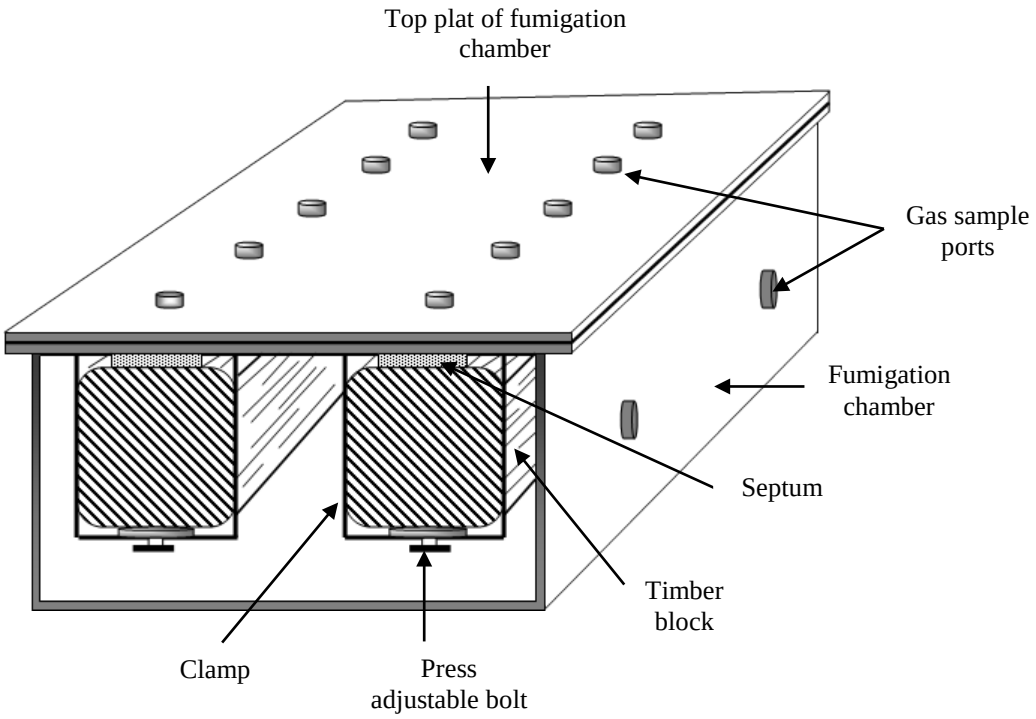
Top plat of fumigation chamber
Gas sample ports
Fumigation chamber
Septum
Timber block
Clamp
Press adjustable bolt

Fig. 1

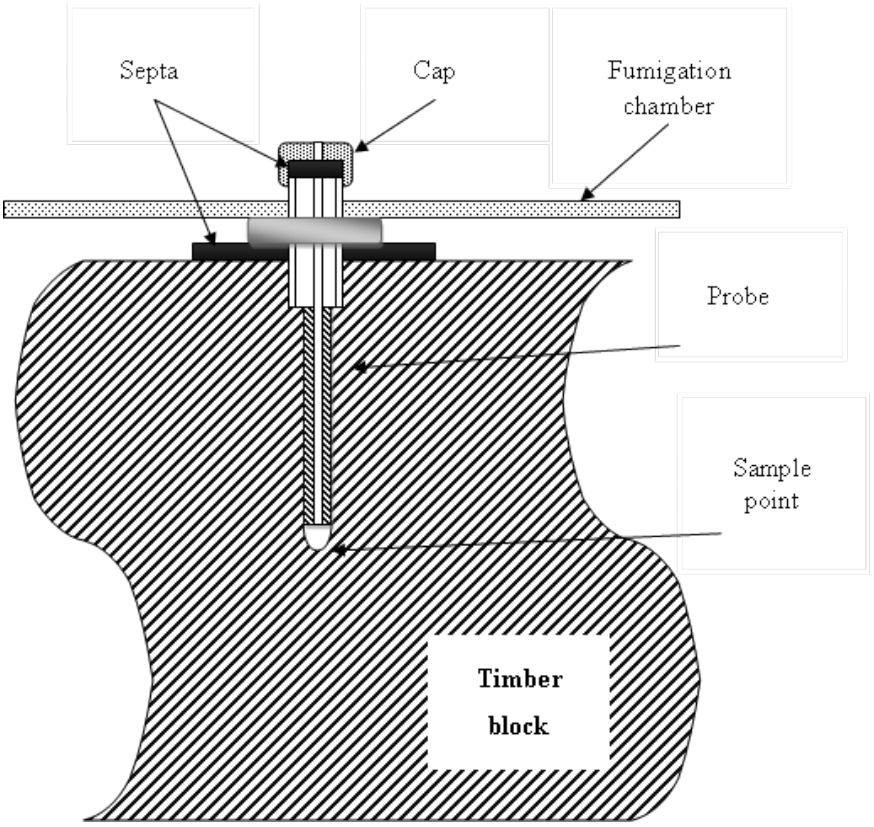
Septa
Cap
Fumigation chamber
Probe
Sample point
Timber block

Fig. 2

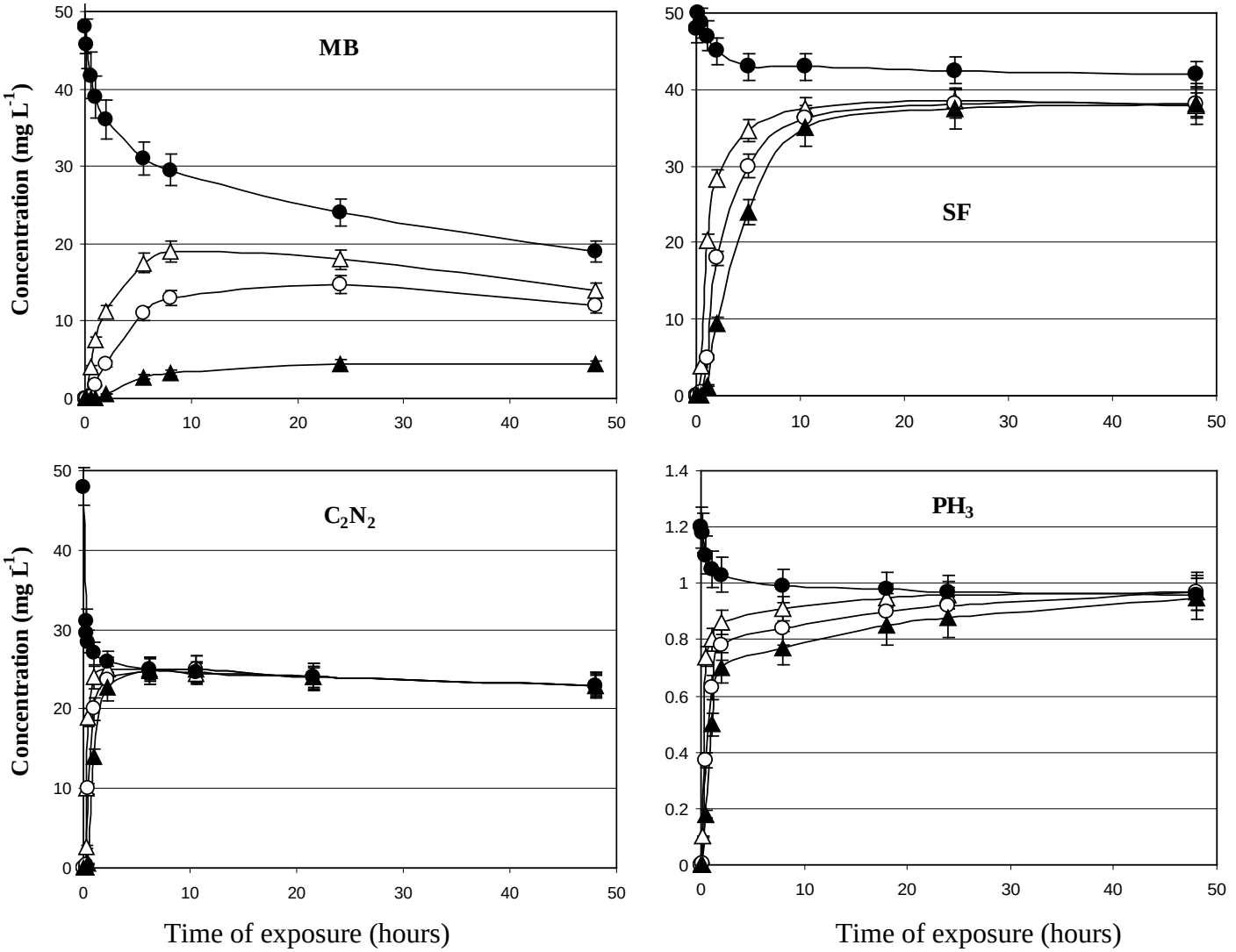
MB
SF
C_2N_2
PH_3
Concentration (mg L^{-1})
Concentration (mg L^{-1})
Time of exposure (hours)
Time of exposure (hours)

Fig. 3

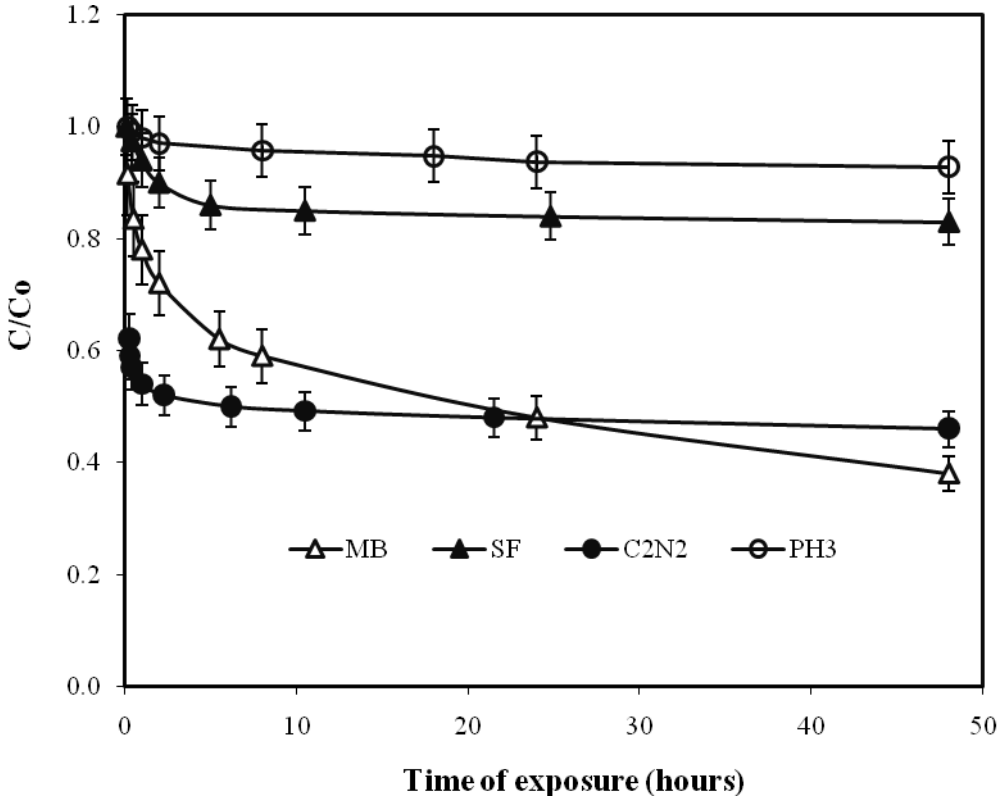
1.2
1.0
0.8
0.6
0.4
0.2
0.0
C/Co
0
10
20
30
40
50
Time of exposure (hours)
MB
SF
C2N2
PH3

Fig. 4

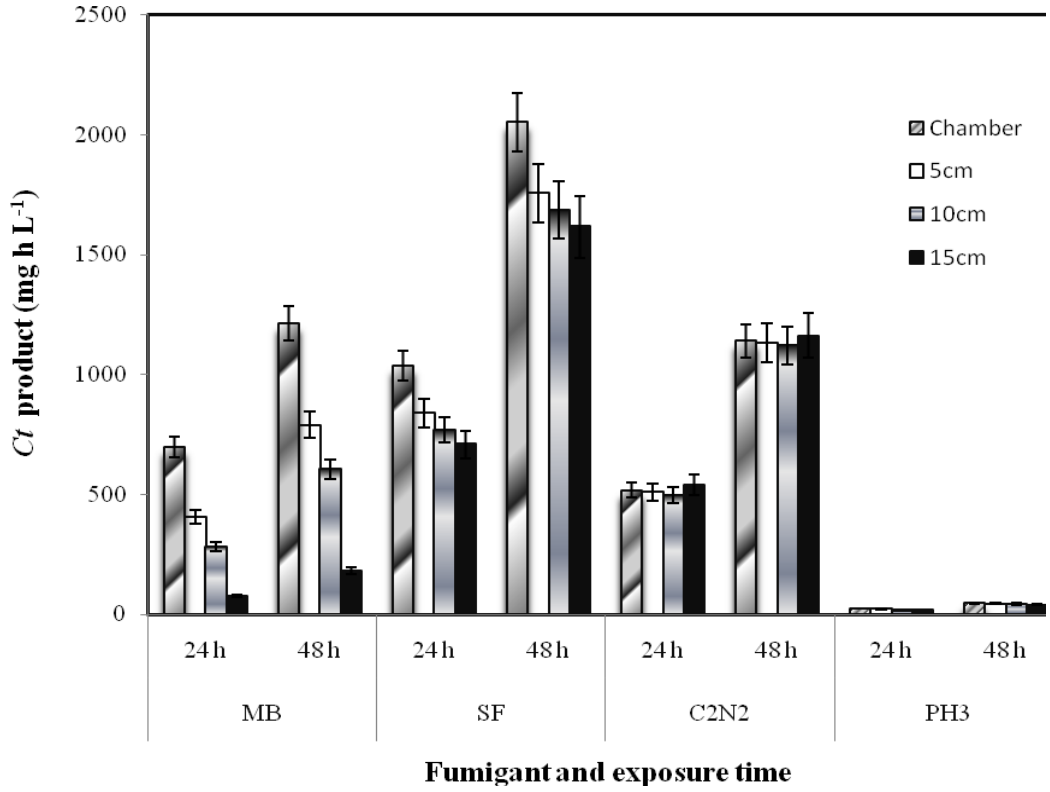
2500
2000
1500
1000
500
0
Ct product (mg h L-1)
Chamber
5cm
10cm
15cm
24 h
48 h
24 h
48 h
24 h
48 h
24 h
48 h
MB
SF
C2N2
PH3
Fumigant and exposure time

Fig. 5.

Fumigant	C*t* product at 48h at distance (mg h L^{-1})		C*t* product required to control (mg h L^{-1})
	5 cm	15cm	*A. glabripennis* (larvae)
MB	789.04[a]	183.08[a]	826 at 10ºC[c] 674 at 21.1ºC[c]
SF	1755.68[a]	1615.80[a]	3279 at 10ºC[c] 1500 at 21.1ºC[c]
C_2N_2	1131.82[a]	1161.54[a]	764 at 10ºC[d] 595 at 21.1ºC[d]
PH_3	44.89[b]	40.48[b]	-

a Without sorption or decomposition, the C*t* product would be 2304 mg h L^{-1}
b Without sorption or decomposition, the C*t* product would be 48 mg h L^{-1}
c Barak, et al., 2002.
d Unpublished trial data (Ren, Y.L)

Table 1.